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(54) POLYLACTATE BIAXIALY STRETCHED LAMINATED FILM HAVING HEAT SEALABILITY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a polylactate biaxially stretched laminated film having excellent transparency, mechanical characteristics and slipperiness and heat sealability, and to provide a method for manufacturing the same.

SOLUTION: The laminated film comprises a base layer (A) made of a polylactate polymer, and a heat sealing layer (B) obtained by blending an anti-blocking agent with a specific biodegradable resin having a void suppressing effect. Alternatively, the laminated film comprises the base layer (A), and the heat sealing layer (B) obtained by blending a surface-treated specific anti-blocking agent with the biodegradable resin and laminated on the layer (A). In the laminated film, the presence ratio of the number of voids having a size of 5 μ m or more per 100 of the anti-blocking agents as seen from the section of the film is 10% or less, and a haze is 10% or less.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the polylactic acid system biaxial-stretching laminated film which has the heat-sealing nature which was excellent in transparency, a mechanical property, or slipping nature especially about the polylactic acid system biaxial-stretching laminated film which has heat-sealing nature, and its manufacture approach.

[0002]

[Description of the Prior Art] Conventionally, polyethylene terephthalate and polypropylene are known as an ingredient excellent in a mechanical strength, thermal resistance, or dimensional stability, and the oriented film using these is broadly used in the industrial world.

[0003] However, if these plastic film has a possibility of damaging an incinerator, during the processing since the calorific value at the time of incineration is high when incineration processing is performed, in case abandonment processing is carried out after the use, and abandonment processing by reclamation is performed, these plastics will remain, without hardly decomposing for chemical and biological stability. Therefore, in connection with the rise of the social need to environmental preservation in recent years, the film which consists of resin which has the biodegradability which can be decomposed by a microorganism etc. and has the biodegradability in which composting processing with compost is possible is demanded. Also in biodegradability resin, polylactic acid is the raw material of the vegetable origin which carried out the polymerization of the lactic acid obtained by fermenting in various starch, a saccharide, etc., and is beginning to be used for various applications as an ideal polymer raw material by which finally serves as carbon dioxide gas and water again, and environmental recycle is carried out on a scale of terrestrial.

[0004] However, it has the property in which polylactic acid is hard and it is weak, and the non-oriented film or sheet which consists of polylactic acid has reinforcement and low ductility, and since it is inferior to shock resistance, if it remains as it is, it runs short of the practicality as a Plastic solid.

[0005] Then, in order to improve the brittleness of polylactic acid, biaxial stretching is carried out and one shaft or the approach of carrying out orientation is learned, and generally, in order to aim at improvement and an improvement of a mechanical strength and impact strength, it is film-ized by biaxial-stretching processing. Although polylactic acid system resin is that biaxial-stretching processing is performed, the effectiveness is great and thickness precision also improves according to draw magnification. If an anti blocking agent is blended in order to give the slipping nature required of this oriented film, when the amount of heat of fusions will carry out biaxial stretching of the polylactic acid system resin of high crystallinity which is 20 or more J/g. Depending on the class of anti blocking agent blended, a big opening generates around an anti blocking agent, the so-called void occurs, and there is a problem of the transparency of a film falling as a result or causing the Hayes unevenness.

[0006] Moreover, although the polylactic acid system biaxial-stretching laminated film was developed by the information record ingredient (magnetic card), the industrial use package, the multifilm for agriculture, etc. and the part has resulted in utilization, the expansion to the field centering on a food packing application is expected from now on.

[0007] Since heat sealing is usually adopted as the seal approach of contents in many cases when applying a polylactic acid system biaxial-stretching laminated film to a food packing application, heat-sealing nature is strongly required of such a film. So, an unstretched film is laminated as sealant

material through adhesives in the oriented film which consists of polylactic acid, and the film which gave heat-sealing nature is indicated by JP,10-100353,A. However, although heat-sealing nature satisfies this film, neither the fall of the impact strength by the brittleness of an unstretched film nor the fall of the transparency by the different-species polymer blend is avoided, but has the problem that an application is easy to be limited. Moreover, since the production process is complicated, it becomes a great energy loss from a viewpoint of saving-resources-izing of energy saving, a film loss, etc.

[0008] Moreover, in addition to this, the biaxially oriented film which has heat-sealing nature in JP,8-323946,A, JP,10-151715,A, etc. is indicated. Although related with the multilayer film which the biaxially oriented film given in JP,8-323946,A used as the base material layer the biaxially oriented film which consists of a polylactic acid system polymer, and made the outer layer the different species material of the low-melt point point which is a heat sealing layer, and carried out the laminating to this base material layer, since that description, therefore transparency fall since crystalline low-melt point point resin is used, or the compatibility of a base material layer and a heat sealing layer differs from ductility greatly, a good thickness precision is hard to be acquired. Moreover, although the biaxially oriented film which constituted the heat-sealing layer from amorphous polylactic acid is indicated by JP,10-151715,A, since the draw magnification which affects the mechanical property of a film is as low as 4 times, there is a problem of being inferior to a mechanical property. Moreover, there is also no description about the slipping nature needed for a film. Thus, it has only the mechanical property to which any biaxially oriented film can be equal to real use, and does not have only the transparency required of a package application.

[0009]

[Problem(s) to be Solved by the Invention] This invention solves said trouble and offers the polylactic acid system biaxial-stretching laminated film which has the heat-sealing nature excellent in transparency, a mechanical property, and slipping nature, and its manufacture approach.

[0010]

[Means for Solving the Problem] this invention persons result in this invention, as a result of repeating research wholeheartedly, in order to solve the above-mentioned technical problem. This invention is a biaxial-stretching laminated film with the heat-sealing layer (B) used as a base material layer (A) and the outermost layer which has two-layer at least. Namely, a base material layer (A) It consists of a polylactic acid system polymer which makes a subject comparatively the polylactic acid of L-lactic acid and D-lactic acid which is (L-lactic acid) / (D-lactic acid) = 100 / 0 - 94/6 (mol %). A heat-sealing layer (B) the Pori DL-lactic acid which L-lactic acid and D-lactic acid copolymerized at a rate of (L-lactic acid) / (D-lactic acid) = 94 / 6 - 70/30 (mol %) more than 60 mass % Under 100 mass % More polymers of at least one or more sorts chosen from aliphatic series-aromatic polyester, polyester carbonate, and aliphatic series polyester than 0 mass % are included at a rate below 40 mass %. It consists of biodegradability resin which has the melting point or softening temperature of the polylactic acid system polymer which constitutes said base material layer (A) lower 10 degrees C or more than the melting point or softening temperature. To said biodegradability resin, the anti blocking agent whose mean diameter is 0.1-5.0 micrometers 0.01-1 mass % content when it is carried out and a film cross section is seen Let the polylactic acid system biaxial-stretching laminated film with which abundance with a number [of openings] of 5 micrometers or more has the heat-sealing nature characterized by for a path being 10% or less and Hayes being 10% or less per anti blocking agent 100 individuals be a summary.

[0011] This invention is a biaxial-stretching laminated film with the heat-sealing layer (B) used as a base material layer (A) and the outermost layer which has two-layer at least. Moreover, a base material layer (A) It consists of a polylactic acid system polymer which makes a subject comparatively the polylactic acid of L-lactic acid and D-lactic acid which is (L-lactic acid) / (D-lactic acid) = 100 / 0 - 94/6 (mol %). A heat-sealing layer (B) consists of biodegradability resin which makes a subject the polylactic acid which has the melting point or softening temperature of the polylactic acid system polymer which constitutes said base material layer (A) lower 10 degrees C or more than the melting point or softening temperature. To said biodegradability resin, the silica whose mean particle diameter by which the surface water acid radical was blocked is 0.1-5.0 micrometers 0.01-1 mass % content when it is carried out and a film cross section is seen Let the polylactic acid system biaxial-stretching laminated film with which abundance with a number [of openings] of 5 micrometers or more has the heat-sealing nature characterized by for a path being 10% or less and Hayes being 10% or less per anti blocking agent 100 individuals be a summary.

[0012]

[Embodiment of the Invention] The polylactic acid system biaxial-stretching laminated film which has the heat-sealing nature of this invention is a laminated film with the heat-sealing layer (B) used as a base material layer (A) and the outermost layer which has two-layer at least and comes to carry out biaxial stretching. Although combination of an anti blocking agent is needed since it slides on a biaxially oriented film and a sex is required, the so-called opening called void around an anti blocking agent at the time of biaxial stretching occurs, and it becomes easy for the transparency of a film to fall. By then, the thing for which a heat-sealing layer (B) is formed in this invention by the biodegradability resin which has void depressor effect, or a special anti blocking agent is blended with the biodegradability resin which forms a heat-sealing layer (B) When the heat-sealing layer (B) used as the outermost layer is made to contain an anti blocking agent, without blending an anti blocking agent with a base material layer (A) substantially and a film cross section is seen A path is abundance ("void content" is called hereafter.) with a number [of openings] of 5 micrometers or more to per anti blocking agent 100 individuals. Generating of a void was controlled so that it might become 10% or less, and the laminated film excellent in the transparency whose Hayes is 10% or less is realized.

[0013] The detail is explained for the laminated film which blended the special anti blocking agent with the 1st laminated film and a heat-sealing layer (B) for the laminated film which constituted the heat-sealing layer (B) from biodegradability resin which has the depressor effect of a void hereafter as the 2nd laminated film.

[0014] The base material layer (A) which is a configuration common to the 1st laminated film and 2nd laminated film needs to consist of polylactic acid system polymers which make a subject comparatively the polylactic acid of L-lactic acid and D-lactic acid which is (L-lactic acid) / (D-lactic acid) = 100 / 0 - 94/6 (mol %). If the content of D-lactic acid occupied to polylactic acid exceeds six-mol %, a polylactic acid system polymer will stop showing the clear melting point, and will become crystallinity with a scarce thing. consequently, the thickness precision at the time of extension -- remarkable -- getting worse -- in addition -- and since orientation crystallization by the heat set after extension will not advance, the problem that lack of a mechanical strength and control of the rate of a heat shrink become difficult arises. Moreover, although L-lactic acid may be used independently, crystallinity is eased for the way where D-lactic acid is blended, and the good thing of film production nature is obtained. Therefore, in this invention, it is more desirable that L-lactic acid and D-lactic acid are blended in (L-lactic acid) / (D-lactic acid) = 99 / 1 - 97/3 (mol %). In addition, as long as L-lactic acid and D-lactic acid are blended at an above-mentioned rate, they may be a copolymer or may be a blend object.

[0015] A urethane bond, amide association, ether linkage, etc. can be introduced into the polylactic acid system polymer which forms a base material layer (A) in the range which does not affect biodegradability. Moreover, as for the number average molecular weight of a polylactic acid system polymer, it is desirable that it is in the range of 50,000-300,000, and it is 80,000-150,000 more preferably. The film obtained as number average molecular weight is less than 50,000 becomes a thing inferior to a mechanical strength, and cutting at an extension process or a rolling-up process also takes place frequently, and it causes an operable fall. On the other hand, if number average molecular weight exceeds 300,000, the fluidity at the time of heating melting will become scarce, and film production nature will fall.

[0016] In order to improve slipping nature, the organic lubricant represented by a below-mentioned anti blocking agent, octadecanamide, etc. may be blended with a base material layer (A) in the range which does not spoil the property, but as for an anti blocking agent, not containing is desirable, in order to control generation of a void and to aim at improvement in transparency.

[0017] Next, the heat-sealing layer (B) arranged at the outermost layer is explained. The heat-sealing layer (B) which constitutes the 1st laminated film is formed by the biodegradability resin which has the depressor effect of a void. This biodegradability resin needs to have the melting point or softening temperature of the polylactic acid system polymer which constitutes a base material layer (A) lower 10 degrees C or more than the melting point or softening temperature. Although mechanical strength is acquired as the difference of the melting point of biodegradability resin or softening temperature, the melting point of the polylactic acid system polymer which constitutes a base material layer (A), or softening temperature is less than 10 degrees C, the temperature which can be heat sealed becomes high and is inferior to heat-sealing nature.

[0018] With the biodegradability resin which has the depressor effect of a void The Pori DL-lactic acid

which L-lactic acid and D-lactic acid specifically copolymerized at a rate of (L-lactic acid) / (D-lactic acid) = 94 / 6 - 70/30 (mol %), At least one or more sorts of polymers chosen from aliphatic series polyester other than polylactic acid, aliphatic series polyester carbonate, and aliphatic series-aromatic polyester ("specific polyester" is called hereafter.) It is biodegradability resin blended at a specific rate. The Pori DL-lactic acid copolymerized at an above-mentioned rate is polylactic acid of low crystallinity, and since it does not show the clear melting point substantially but becomes easy to flow, it not only can raise the heat-sealing nature in low temperature, but it comes to discover high void depressor effect. Moreover, by blending specific polyester further in addition to this Pori DL-lactic acid of low crystallinity, the crystallinity of polylactic acid is eased more and depressor effect of a high void and improvement in heat-sealing nature can be aimed at. However, since adhesion with a base material layer (A) not only falls, but it is in the inclination for transparency to fall when specific polyester is blended too much so much, it is necessary to make more blending ratio of coal of specific polyester than 0 mass % below into 40 mass % for the blending ratio of coal of the Pori DL-lactic acid of low crystallinity under 100 mass % more than 60 mass %.

[0019] In addition, the heat-sealing nature in the low temperature in this invention is heat-sealing nature which has good heat-sealing nature in a film comrade's lamination in the temperature of 100-140 degrees C, and has the heat-sealing reinforcement of 3 or more N/cm more preferably. It can be used suitable for a package of the lightweight object [be / it / what has such heat-sealing nature] centering on overlapping.

[0020] To the biodegradability resin which has the depressor effect of the void constituted as mentioned above, the anti blocking agent whose mean diameter is 0.1-5.0 micrometers needs to contain in the range of 0.01 - 1 mass %. If sufficient slipping nature or abrasion resistance are not not only obtained, but the blended anti blocking agent may drop out of a film if the mean particle diameter of an anti blocking agent is smaller than 0.1 micrometers, and the mean particle diameter of an anti blocking agent exceeds 5.0 micrometers, a film front face will become extremely coarse and transparency will fall. Therefore, as for the mean particle diameter of an anti blocking agent, it is more desirable that it is in the range of 0.5-3 micrometers. Moreover, if there is less blending ratio of coal of an anti blocking agent than 0.01 mass %, sufficient slipping nature or abrasion resistance will not be obtained, but if the blending ratio of coal of an anti blocking agent exceeds 1 mass %, a film front face will become extremely coarse and transparency will fall. Therefore, as for the blending ratio of coal of an anti blocking agent, it is more desirable that it is the range of 0.05 - 0.5 mass %.

[0021] The so-called organic system bead which covered stable metal salts, such as stable metallic oxides, such as a silica, a titanium dioxide, and an alumina, a calcium carbonate, calcium phosphate, and a barium sulfate, or polylactic acid system resin with inactive organic resin as an anti blocking agent in this invention is mentioned, and a silica can use it suitably even especially in inside. These anti blocking agents may use one kind independently, and may use two or more sorts together.

[0022] As aliphatic series polyester other than the polylactic acid in this invention, polyethylene succinate, a polyethylene horse mackerel peat, a polyethylene RENSUBE rate, polyethylene sebacate, a polyethylene decane dicarboxy rate, polybutylene succinate, a polybutylene horse mackerel peat, polybutylene sebacate, and these copolymers are mentioned, for example. Especially, polybutylene succinate and a polybutylene succinate horse mackerel peat are used suitably. Moreover, in this invention, the block copolymer (the product which contained an ester interchange product and little chain elongation agent residue in part is also included) of a polylactic acid system polymer and aliphatic series polyester can also be used. This block copolymer can be adjusted by the approach of arbitration.

[0023] As aliphatic series-aromatic polyester in this invention That what is necessary is just what has an aliphatic series component and an aromatic series component For example, a lactic acid, Hydroxy caproic acids, such as a glycolic acid, hydroxybutyric acid, and a hydroxy caproic acid Annular lactone, such as a caprolactone, a butyrolactone, a lactide, and glycolide Ethylene glycol, butanediol, cyclohexane dimethanol, Diols, such as screw-hydroxy methylbenzene and toluene diol Dicarboxylic acid, such as a succinic acid, an adipic acid, a suberic acid, a sebacic acid, a terephthalic acid, isophthalic acid, and naphthalene dicarboxylic acid, cyclic anhydrides, and oxiranes are used as a component, and the copolymer which has an aliphatic series component and an aromatic series component is mentioned. Especially, 1,4-butanediol and the copolymerized polyester which has a terephthalic acid as an adipic acid and an aromatic series component are desirable as an aliphatic series component. Moreover, a urethane bond, amide association, ether linkage, etc. can also be introduced in the range which does not

affect biodegradation.

[0024] What is obtained as polyester carbonate in this invention by making a dihydroxy compound, dicarboxylic acid, its alkyl ester, or a dihydroxy compound and carbonic acid diester react can be used.

[0025] It is desirable for ethylene glycol, a trimethylene glycol, tetramethylene glycol, butanediol, pentanediol, a BUROPIREN glycol, hexamethylene glycol, neopentyl glycol, toluene diol, screw-hydroxy methylbenzene, etc. to be mentioned, and to use 1,4-butanediol as one sort of a component especially as a dihydroxy compound, for example. As dicarboxylic acid, a malonic acid, a glutaric acid, an adipic acid, an azelaic acid, a terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, etc. can be suitably used together, for example. Especially, it is desirable to use a succinic acid as one sort of a component. In addition, a dihydroxy compound and dicarboxylic acid may be these ester or an acid anhydride. Moreover, a dihydroxy compound and dicarboxylic acid have the desirable thing of the melting point with extent high respectively independently, although it can use as mixture and desired combination is possible which has moderate biodegradability and can realize practical thermal resistance in this invention. Moreover, it is desirable that 1,4-butanediol is included as a dihydroxy compound and a succinic acid is included as dicarboxylic acid. As carbonic acid diester, dimethyl carbonate, diethyl carbonate, diisopropyl carbonate, dibutyl carbonate, diphenyl carbonate, ditolyl carbonate, bis(chlorophenyl) carbonate, m-cresyl carbonate, etc. can be mentioned, and diphenyl carbonate is desirable also in especially inside.

[0026] As for the heat-sealing layer (B) which constitutes the 2nd laminated film, it comes to blend a special anti blocking agent with biodegradability resin. It will not be limited especially if biodegradability resin here is biodegradability resin which makes a subject the polylactic acid which has the melting point or softening temperature of the polylactic acid system polymer which constitutes a base material layer (A) lower 10 degrees C or more than the melting point or softening temperature in order to demonstrate good heat-sealing nature and to secure adhesion with a base material layer (A).

[0027] As a special anti blocking agent blended with this biodegradability resin, the silica by which the surface water acid radical was blocked is used, and the silica by which the surface water acid radical was especially blocked by the silane coupling agent can use it suitably. Although it is desirable that 20% or more of the surface water acid radical is blocked by the silane coupling agent as for a silica, since it is in the inclination which the rate that a silane coupling agent exists in a film in the free condition increases, and causes nebula and the fish eye of a film when the rate of a blockade of a surface water acid radical exceeds 80%, considering as 80% is suitable for the upper limit.

[0028] As a silane coupling agent used by this invention, the compound expressed with a chemical formula YRSiX_3 is pointed out. Here, an alkyl group and X of organic functional groups, such as an epoxy group, an amino group, an methacrylic radical, and a vinyl group, and R are hydrolysis nature machines, such as an alkoxy group, an acetoxyl radical, and the Krol radical, and, specifically, Y is gamma-glycidoxypopyltrimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-methacryloxypropyl trimethoxy silane, vinyltriethoxysilane, vinyl trichlorosilan, etc. Although it is not restricted and well-known approaches, such as the pretreating methods, the integral blending methods, etc., such as a ** type method, slurry method, and a spray method, can be adopted especially as the surface treatment approach by said silane coupling agent of a silica, the pretreating method for the ability to process a silica front face to homogeneity is desirable.

[0029] The mean particle diameter of the silica by which the surface water acid radical was blocked needs to be 0.1-5.0 micrometers, and the blending ratio of coal needs to be 0.01 to 1 mass %. If the mean particle diameter of a silica is smaller than 0.1 micrometers, sufficient slipping nature or abrasion resistance are not only obtained, but the blended silica may drop out of a film. Moreover, if the mean particle diameter of a silica exceeds 5.0 micrometers, a film front face will become extremely coarse and transparency will fall. Therefore, as for the mean particle diameter of the silica to which surface treatment was performed, it is more desirable that it is in the range of 0.5-3 micrometers. Moreover, if there is less blending ratio of coal of a silica to which surface treatment was performed than 0.01 mass %, sufficient slipping nature or abrasion resistance will not be obtained, but if the blending ratio of coal of a silica exceeds 1 mass %, a film front face will become extremely coarse and transparency will fall. Therefore, as for the blending ratio of coal of the silica by which the surface water acid radical was blocked, it is more desirable that it is the range of 0.05 - 0.5 mass %.

[0030] Thus, the silica to which surface preparation was performed is used as an anti blocking agent, by blending with the biodegradability resin which forms a heat-sealing layer (B), compatibility with the

resin which constitutes an anti blocking agent, a heat-sealing layer (B), or a base material layer (A) is raised more, the extension imitation nature at the time of performing extension processing like the after-mentioned improves, and the amount of void generation can be controlled further.

[0031] In the 1st and 2nd laminated film in this invention, especially the method of making biodegradability resin contain an anti blocking agent is not limited, and can adopt a well-known approach. For example, high concentration is made to knead and masterbatch-size biodegradability resin and an anti blocking agent in a twin screw extruder, and the approach of blending and making it dilute with the biodegradability resin which does not contain an anti blocking agent at the time of extrusion is mentioned. Moreover, the approach of combining an anti blocking agent at the time of the polymerization of biodegradation resin is also applicable. Even if it makes either contain an anti blocking agent, you may make it contain in each resin beforehand, when two or more sorts of biodegradability resin is mixed. The mean particle diameter and the addition of an anti blocking agent to blend are suitably adjusted according to military requirements, such as thickness of a heat-sealing layer (B), and transparency, slipping nature.

[0032] In the 1st and 2nd base material layer (A) and heat-sealing layer (B) of a laminated film, a pigment, an antioxidant, a plasticizer, an ultraviolet ray absorbent, lubricant, a crystalline-nucleus agent, an antistatic agent, etc. may be added in the range which does not spoil the property.

[0033] Moreover, although the approach of the 1st and 2nd laminated film producing separately the base material layer (A) and heat-sealing layer (B) which were constituted as mentioned above by for example, the T-die method, the tubular film process, the calender method, etc., and carrying out thermocompression bonding of the obtained oriented film through a binder is also considered Since it becomes cost quantity, it is desirable to manufacture by the so-called co-extruding method which piles up and extrudes a base material layer and a heat-sealing layer within a dice using two or more extruders.

[0034] Moreover, it is desirable the two-layer configuration (A/B) of a base material layer (A) and a heat-sealing layer (B) or to make the 1st and 2nd laminated film into 3 lamination, although which gestalt is sufficient 3 lamination (B/A/B). When it is 3 lamination, since both the outermost layers turn into a heat-sealing layer, it is advantageous also in seal reinforcement also in application, and since slipping nature is fully obtained even if it does not make a base material layer contain an anti blocking agent, it is desirable also from the point of transparency and cost.

[0035] Moreover, although what is necessary is not to limit especially the thickness of the 1st and 2nd laminated film, and just to set it up suitably with an application, a military requirement, a price, etc., it is suitable for it that it is the thickness of about 10-200 micrometers.

[0036] Moreover, in order to give for example, the gas barrier nature other than the heat-sealing layer (B) used as a base material layer (A) and the outermost layer to the 1st and 2nd laminated film, the layer which consists of polyvinyl alcohol etc. may be prepared.

[0037] Furthermore, surface treatment of corona treatment, plasma treatment, the flame treatment, etc. may be carried out to the film front face of the 1st and 2nd laminated film, and the surface treatment of a film is an effective means not only about improvement in printing nature but heat-sealing nature.

[0038] Below, an example is given and explained about the manufacture approach of a polylactic acid system biaxial-stretching laminated film of having the heat-sealing nature of this invention by the co-extruding method. In manufacturing by the T-die method, the co-extrusion which heats the biodegradability resin with which the anti blocking agent which constitutes a heat-sealing layer (B) was blended with the polylactic acid system polymer which constitutes a base material layer (A) with the extruder made into the cylinder temperature of 180-260 degrees C and the T-die temperature of 200-250 degrees C, carries out melting kneading, and uses a heat-sealing layer (B) as the outermost layer performs melting film production. And it cools with the cooling roller controlled by 20-40 degrees C, and a non-extended sheet with a thickness of 100-500 micrometers is obtained.

[0039] As the biaxial-stretching approach of a non-extended sheet, any of the coaxial biaxial-stretching method by the tenter method and the serial biaxial-stretching method by the roll and the tenter are sufficient. For example, in using an unstretched film as a laminating oriented film by the biaxial-stretching method serially, by the rotational-speed ratio of a drive roll, a non-extended sheet is extended to a lengthwise direction with the roll skin temperature of 50-80 degrees C, and it extends it in a longitudinal direction at the extension temperature of 70-100 degrees C continuously succeedingly. Although it is not limited, when a mechanical property, transparency, etc. are taken into consideration, as for especially draw magnification, it is desirable to carry out biaxial stretching of the draw magnification

so that vertical draw magnification and horizontal draw magnification may be 2.5 or more times, respectively and a field scale factor may become 8 or more times. Sufficient mechanical strength is not acquired as vertical draw magnification and horizontal draw magnification are less than 2.5 times, but it is inferior to practicality. Moreover, although especially the upper limit of vertical draw magnification and horizontal draw magnification is not limited, since it will become easy to generate a film tear if 8 times are exceeded, as for vertical draw magnification and horizontal draw magnification, it is desirable that it takes 2.5 or more times for less than 8 times, and it is more desirable that vertical draw magnification is 2.5 times to 5.0 times, and horizontal draw magnification is 2.5 times to 8.0 times.

[0040] After the above-mentioned extension processing is performed, heat treatment is performed at the temperature of 100-150 degrees C, and heat relaxation processing is performed under conditions of 2 - 8% of rates of relaxed. Thus, by making a heat-sealing layer (B) carry out little content of the specific anti blocking agent, and producing a laminated film by co-extrusion, or it constitutes a heat-sealing layer (B) from polylactic acid system resin of low crystallinity with void depressor effect, the void formed in a film plane can be extremely reduced until void content becomes 10% or less. Consequently, Hayes is 10% or less, and it becomes possible to obtain a laminated film with little Hayes unevenness.

[0041] Even if the heat-sealing layer (B) of the outermost layer is extended with a base material layer (A) and a heat set is carried out for orientation crystallization of a base material layer (A), since it is hard to carry out orientation crystallization of the polylactic acid system resin itself which is a subject, it never spoils heat-sealing nature.

[0042] Therefore, the polylactic acid system biaxial-stretching laminated film which has the obtained heat-sealing nature is excellent in transparency, slipping nature, heat-sealing nature, and mechanical physical properties, and since an anti blocking agent is also little and ends, it can obtain the advantageous laminated film also in cost.

[0043] The polylactic acid system biaxial-stretching laminated film which has such heat-sealing nature can be suitably used as wrapping of an overlapping application suitable for an individual package or an accumulation package of food packaging materials, such as a confectionery bag, wrapping, such as drugs, a magnetic tape, a magnetic disk, etc., in addition can be suitably used as wrapping ingredients, such as a bag for a kitchen garbage package, a ***** film of an envelope, and electrical and electric equipment, electronic parts, the film for agriculture, paper, the laminated print laminate film, etc.

[0044]

[Example] Next, although this invention is concretely explained based on an example, this invention is not limited only to these examples. In addition, measurement of the various physical-properties values in an example and the example of a comparison was carried out by the following approaches.

(1) Void content (%) : the film cross section was observed with the electron microscope, and the magnitude of the opening currently generated around an anti blocking agent was read on the photograph. And the path in per anti blocking agent 100 individuals made void content abundance with a number [of openings] of 5 micrometers or more. In this invention, that whose void content is 10% or less was made good.

(2) Hayes (%) : it measured using the full automatic hazemeter (the Tokyo Denshoku Co., Ltd. make, TC-H 111DPK), and calculated based on the following type.

[0045] Hayes (%) = $(T_d/T_t) \times 100$ -- here, $T_d(s)$ are (%) and a luminous diffuse transmittance and T_t is total light transmission (%). In this invention, transparency made good that whose Hayes is 10% or less.

(3) Tensile strength (MPa) : according to the measuring method of ASTM-D882, it measured by the sample with a die length [of 100mm], and a width of face of 10mm. In this invention, the case where the direction of MD and the direction of TD exceeded 130MPa(s) was made good.

(4) Dynamic friction coefficient : it becomes the index of slipping nature and is JIS. According to the approach of a publication, a film comrade's dynamic friction coefficient was measured to K-7125. And it slid on that whose dynamic friction coefficient is 0.60 or less, and the sex presupposed that it is good.

(5) Heat-sealing reinforcement (N/15mm) : using the heat sealer made from circuit tester industry, at the temperature of 100 degrees C, 120 degrees C, and 140 degrees C, the front flesh-side comrade of a film was piled up under the conditions for 0.1MPa x 1 second, and thermal melting arrival of the seal bar with a width of face of 10mm was carried out for the film sample started in a width of 15mm, and die length of 150mm. It is JIS about the obtained heat seal sample. According to the approach of a publication, T mold friction test was performed to K-6854 at the exfoliation rate of 300 mm/min, and the maximum stress at the time of exfoliation was made into heat-sealing reinforcement. And heat-sealing

reinforcement presupposed that what is 3Ns / 15mm or more is excelled in heat-sealing nature.

(6) The rate of a blockade of a silica hydroxyl group (%) : the silica was returned by the lithium and the aluminum hydride and the generated amount of hydrogen was computed by the gas-chromatography method.

[0046] As a polymer which constitutes a rate (%) of hydroxyl-group blockade =(amount of hydroxyl groups before amount of hydroxyl groups / processing after processing) x100 example 1 base-material layer (A), the melting point used the polylactic acid (the Cargill Dow polymer company make) which is L-lactic acid / D-lactic-acid =99 / 1 (mol %) at 166 degrees C.

[0047] Moreover, polylactic acid (Cargill Dow polymer company make) 90 mass % whose melting points are L-lactic acid / D-lactic-acid =92 / 8 (mol %) at 130 degrees C, and aliphatic series polyester (Showa High Polymer Co., Ltd. make, Bionolle #1903) 10 mass % whose melting point is 115 degrees C were used as a polymer which constitutes a heat-sealing layer (B). The polymer which made this polymer contain indeterminate form silica (Fuji SHIRISHIA chemistry company make, SAIRISHIA 310P) 0.1 mass % whose mean particle diameter is 1.4 micrometers as an anti blocking agent was used.

[0048] And the cast roll with which each polymer was fused and temperature control of a co-extrusion and the skin temperature was carried out to 25 degrees C at the T-die temperature of 220 degrees C was made to carry out adhesion quenching, and the non-extended sheet with a thickness of 360 micrometers was produced so that a heat-sealing layer (B) might be formed in both sides of a base material layer (A). In consideration of the below-mentioned draw magnification, the amount of extrusion of a polymer was adjusted so that film thickness might finally be set to heat-sealing (layer B) / base material (layer A) / heat-sealing (layer B) =5/20/5 (micrometer).

[0049] The obtained non-extended sheet was serially supplied to the biaxial drawing machine, it extended 3.5 times to the lengthwise direction beforehand under 60 degrees-C [of hot calender rolls], and extension roll 75 degree C conditions, and extension processing was succeedingly performed 4.5 times in the longitudinal direction under extension roll 80 degree C conditions. Then, it heat-treated at 125 degrees C, having used the lateral rate of relaxation as 4%, corona treatment was performed to one field, and the laminating oriented film with a thickness of 30 micrometers was obtained.

[0050] The physical properties of the obtained laminated film etc. are shown in Table 1.

[0051]

[Table 1]

		実施例 1	実施例 2	実施例 3	実施例 4	実施例 5
組成	基材層(A)	A-1	A-1	A-2	A-2	A-1
	ヒートシール層(B) (質量%)	B-1/B-2 90/10	B-1/B-3 80/20	B-1/B-4 70/30	B-1 100	B-1 100
	アブローガ剤(C) (質量%)	C-1 0.1	C-1 0.03	C-2 0.05	C-3 0.1	C-4 0.05
製造 条件	延伸倍率 縦	3.5	4.0	4.0	4.0	3.0
	横	4.5	5.0	5.0	5.0	4.0
物性	ボイド含有率(%)	5	4	3	1	2
	ヘイズ (%)	4.1	3.8	3.5	2.3	4.8
	引張強度(MPa) MD	163	160	172	175	153
		ID	185	192	210	182
	動摩擦係数	0.52	0.50	0.44	0.48	0.47
	ヒートシール強度(N/cm)	100℃	9.5	7.5	11.0	8.5
		120℃	14.0	12.5	14.0	13.0
		140℃	16.5	14.0	16.0	13.0

A-1: ポリ乳酸 カギル・ダウ・ポリマ-社製 D体1%, 融点166℃

A-2: ポリ乳酸 カギル・ダウ・ポリマ-社製 D体4%, 融点151℃

B-1: ポリ乳酸 カギル・ダウ・ポリマ-社製 D体8%, 融点130℃

B-2: 脂肪族ポリエステル 昭和化学工業社製 ビオノール #1903, 融点115℃

B-3: ポリイソブチレン 三菱化学工業社製 IUPBC550, 融点97℃

B-4: 脂肪族芳香族共重合ポリエステル BASF社製, コルックSE, 融点105℃

C-1: 不定形シリカ 富士シリカ化学社製 サイリシア310P, 平均粒径1.4μm

C-2: 不定形シリカ 富士シリカ化学社製 サイリシア730P, 平均粒径3.0μm

C-3: C-1の水酸基を50%封鎖処理したシリカ

C-4: C-1の水酸基を100%封鎖処理したシリカ

As a polymer which forms an example 2 heat-sealing layer (B), polylactic acid (Cargill Dow polymer company make) 80 mass % whose melting points are L-lactic acid / D-lactic-acid = 92 / 8 (mol %) at 130 degrees C, and polyester carbonate (Mitsubishi Gas Chemical [Co., Inc.] make: IUPEC 550) 20 mass % whose melting point is 97 degrees C were used. Moreover, it was made as 4.0 times in the lengthwise direction, and draw magnification at the time of extension was made into 5.0 times in the longitudinal direction. And the laminating oriented film was produced like the example 1 except it. [0052] The physical properties of the obtained laminated film etc. are shown in Table 1.

As a polymer which constitutes an example 3 base-material layer (A), the melting point used the polylactic acid (the Cargill Dow polymer company make) which is L-lactic acid / D-lactic-acid = 96 / 4 (mol %) at 151 degrees C. The melting point as a polymer which forms a heat-sealing layer (B) moreover, at 130 degrees C L-lactic acid / D-lactic acid = Polylactic acid (Cargill Dow polymer company make) 70 mass % which is 92/8 (mol %), The thing which made aliphatic series-aromatic series copolymerized polyester (BASF A.G. make, Eko FREX F) 30 mass % whose melting point is 105 degrees C contain indeterminate form silica (Fuji SHIRISHIA chemistry company make, SAIRISHIA 730) 0.05 mass % whose mean particle diameter is 3.0 micrometers as an anti blocking agent was used. Furthermore, it was made as 4.0 times in the lengthwise direction, and draw magnification at the time of extension was made into 5.0 times in the longitudinal direction. And the laminating oriented film was produced like the example 1 except it.

[0053] The physical properties of the obtained laminated film etc. are shown in Table 1.

As a polymer which constitutes an example 4 base-material layer (A), the melting point used the polylactic acid (the Cargill Dow polymer company make) which is L-lactic acid / D-lactic-acid = 96 / 4 (mol %) at 151 degrees C. Moreover, the silica which carried out blockade processing of the hydroxyl group of the indeterminate form silica (the Fuji SHIRISHIA chemistry company make, SAIRISHIA 310P) whose mean particle diameter is 1.4 micrometers 50% by gamma-glycidoxypopyltrimetoxysilane was used for the anti blocking agent which a heat-sealing layer (B) is made to contain. Furthermore, it was made as 4.0 times in the lengthwise direction, and draw magnification at the time of extension was made into 5.0 times in the longitudinal direction. And the laminating oriented film was produced like the example 1 except it.

[0054] The physical properties of the obtained laminated film etc. are shown in Table 1.

As an anti blocking agent blended with an example 5 heat-sealing layer (B), mean particle diameter made the blending ratio of coal 0.05 mass % using the silica which carried out blockade processing of the hydroxyl group of the indeterminate form silica (the Fuji SHIRISHIA chemistry company make, SAIRISHIA 310P) which is 1.4 micrometers 100% by gamma-glycidoxypopyltrimetoxysilane. And the laminating oriented film was produced like the example 1 except it.

[0055] The physical properties of the obtained laminated film etc. are shown in Table 1. Examples 1-3 are formed in the polylactic acid system polymer with which the base material layer (A) was blended at a rate of specification [L-lactic acid and D-lactic acid]. The heat-sealing layer (B) is formed by the biodegradability resin which has the void depressor effect by which specific polyester was blended with crystalline low polylactic acid. Since the anti blocking agent which has the mean diameter of this invention contained at a rate of this invention within the limits in the heat-sealing layer (B), void content is as low as 10% or less, Hayes becomes 10% or less, all are excellent in transparency, and the good thing of slipping nature was obtained. Moreover, the heat-sealing layer (B) is formed by the biodegradability resin which has the melting point lower 10 degrees C or more than the melting point of the polylactic acid system polymer which constitutes a base material layer (A). While the laminating of a base material layer (A) and the heat-sealing layer (B) is carried out by co-extrusion Since extension processing was performed by the suitable draw magnification in this invention, the adhesion of a base material layer (A) and a heat-sealing layer (B) became good, and the laminated film which is powerfully [mechanically] excellent and has the outstanding heat-sealing reinforcement was obtained.

[0056] Moreover, it replaced with the configuration of the heat-sealing layer (B) of the above-mentioned examples 1-3, and the same effectiveness as each above-mentioned example was acquired also in the examples 4 and 5 which formed the heat-sealing layer (B) by the biodegradability resin which blended the silica by which surface treatment was carried out as an anti blocking agent. In addition, the example 5 was not what affects transparency, although the bleed out of some finishing agent arose and Hayes became high, since there were more rates of processing of the surface water acid radical of a silica than

the suitable range in this invention.

As a polymer which constitutes an example of comparison 1 base-material layer (A), the melting point used the polylactic acid (the Cargill Dow polymer company make) which is L-lactic acid / D-lactic-acid =92 / 8 (mol %) at 130 degrees C. Moreover, the melting point used the polylactic acid (the Cargill Dow polymer company make) which is L-lactic acid / D-lactic-acid =99 / 1 (mol %) at 166 degrees C as a polymer which constitutes a heat-sealing layer (B). And the laminating oriented film was produced like the example 1 except it.

[0057] The physical properties of the obtained laminated film etc. are shown in Table 2.

[0058]

[Table 2]

		比較例 1	比較例 2	比較例 3	比較例 4
組成	基材層(A)	B-1	A-1	A-1	B-2
	ヒートシール層(B)	A-1	B-1	B-1	B-1
	(質量%)	100	100	100	100
製造 条件	アガロシカゲ剤(C)	C-1	C-1	C-1	C-1
	(質量%)	0.1	2	0.005	0.1
	延伸倍率 縦	3.0	3.0	3.0	3.0
物性	横	4.0	4.0	4.0	4.0
	ボイド含有率(%)	13	15	1	7
	ヘイズ (%)	11.0	13.0	1.6	11.2
	引張強度(MPa) MD	90	150	162	80
	TD	113	171	208	90
	動摩擦係数	0.51	0.42	0.75	0.56
	100℃	0.5	7.5	8.0	7.2
	ヒートシール強度(N/cm) 120℃	1.0	12.0	12.5	11.6
	140℃	1.5	14.0	14.5	13.3

A-1: ポリ乳酸 カギル・ダウ・ポリマー社製 D体1%, 融点166℃

B-1: ポリ乳酸 カギル・ダウ・ポリマー社製 D体8%, 融点130℃

B-2: 脂肪族ポリエステル 昭和化学工業社製ビオノール#1903, 融点115℃

C-1: 不定形カゲ剤 富士シリシア化学社製サリカ310P, 平均粒径1.4μm

More blending ratio of coal of the anti blocking agent blended with an example of comparison 2 heat-sealing layer (B) than the rate of this invention was made into 2 mass %. And the laminating oriented film was produced like the example 1 except it.

[0059] The physical properties of the obtained laminated film etc. are shown in Table 2.

The blending ratio of coal of the anti blocking agent blended with an example of comparison 3 heat-sealing layer (B) was made into 0.005 mass % fewer than the rate of this invention. And the laminating oriented film was produced like the example 1 except it.

[0060] The physical properties of the obtained laminated film etc. are shown in Table 2.

As a polymer which constitutes an example of comparison 4 base-material layer (A), the aliphatic series polyester (the Showa High Polymer Co., Ltd. make, Bionolle #1903) whose melting point is 115 degrees C was used. And the laminating oriented film was produced like the example 1 except it.

[0061] The physical properties of the obtained laminated film etc. are shown in Table 2. Since the example 1 of a comparison had the melting point of a heat-sealing layer (B) higher than the melting point of a base material layer (A), it was not what is inferior to heat-sealing strength and can be equal to real use. Moreover, highly, void content became high and the crystallinity of a heat-sealing layer (B) became that in which the Hayes value is inferior to transparency highly.

[0062] Since the example 2 of a comparison had more blending ratio of coal of an anti blocking agent than the range of this invention, void content became high and the Hayes value became what is highly inferior to transparency. Since the example 3 of a comparison had less blending ratio of coal of an anti blocking agent than the range of this invention, it became that in which a dynamic friction coefficient is inferior to slipping nature highly.

[0063] Since the base material layer (A) was formed not with a polylactic acid system polymer but with ***** polyester, the example 4 of a comparison became a thing inferior to transparency and tensile strength.

[0064]

[Effect of the Invention] According to the polylactic acid system biaxial-stretching laminated film which has the heat-sealing nature of this invention as mentioned above By forming a base material layer (A) for the laminated film which consists of a base material layer (A) and a heat-sealing layer (B) in a polylactic acid system polymer, and forming a heat-sealing layer (B) by the biodegradability resin of low crystallinity with void depressor effect When the obtained film looks at a film cross section, a path becomes [abundance with a number / of openings / of 5 micrometers or more] as small as 10% or less per anti blocking agent 100 individuals, and the laminated film Hayes excelled [laminated film] in 10% or less and transparency is obtained. Furthermore, since the loadings of an anti blocking agent are also little and end, the advantageous laminated film also in cost can be obtained.

[0065] Or also by replacing with the configuration of the above-mentioned heat-sealing layer (B), blending the silica by which the surface water acid radical was blocked by biodegradability resin as an anti blocking agent, and constituting a heat-sealing layer (B), the depressor effect of a void is acquired, it excels in transparency and the laminated film which combines heat-sealing nature and slipping nature as it is mechanically powerful is obtained.

[0066] Such a laminated film can be suitably used as overlapping wrapping suitable for an individual package or an accumulation package of food packaging materials, such as a confectionery bag, wrapping, such as drugs, a magnetic tape, a magnetic disk, etc.

[Translation done.]